Tetrahedron Letters, Vol.31, No.46, pp 6713-6716, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

A SIMPLE AND EFFICIENT SYNTHESIS OF 2-AMINO-1,3-BUTADIENES FROM β-ENAMINO PHOSPHONIUM SALTS

José BARLUENGA *, Isabel MERINO and Francisco PALACIOS.

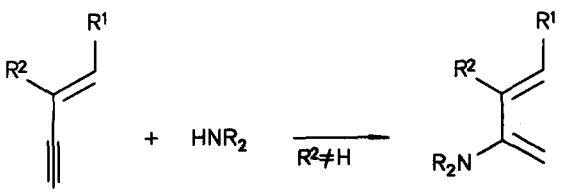
Departamento de Química Organometálica. Facultad de Química.
Universidad de Oviedo. 33071 Oviedo. Spain.

SUMMARY: A new and very simple synthesis of 2-amino-1,3-butadienes is described through Wittig reaction of the phosphoranes generated *"in situ"* from the β-enamino phosphonium salts with aldehydes.

Compounds containing the 1,3-butadiene with attached heteroatom substituents represent a very important class of derivatives as a result of their potential as key intermediates in organic synthesis. Particularly significant is the Diels-Alder reactivity of these substances with electron donating substituents in 2-position for the construction of functionalized cyclohexene derivatives [1].

Synthesis and reactions of 2-alkoxy- or 2-siloxy-1,3-butadienes [2], as well as sulfur-substituted dienes such as 2-phenylthio-[3] or phenylsulfonyl-1,3-butadienes [4] have attracted a great deal of interest in recent years. However, the corresponding 2-amino-1,3-butadienes has been scarcely studied, probably owing to the lack of general methods of preparation of these type of compounds.

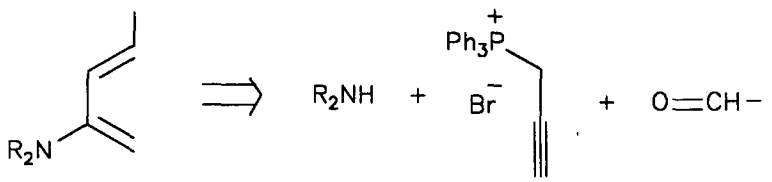
In this context, we have shown that 2-amino-1,3-butadienes are versatile reagents in [4+2] cycloaddition processes as well as other reactions [5]. However, the catalytic aminomercuriation of en-ynes [6] used for the preparation of aminodiene 3 was restricted to the synthesis of the 3-alkyl substituted derivatives 3 and when alk-3-en-1-ynes (1, R^2=H) were used they underwent Michael addition of a second molecule of amine.



1 2 3

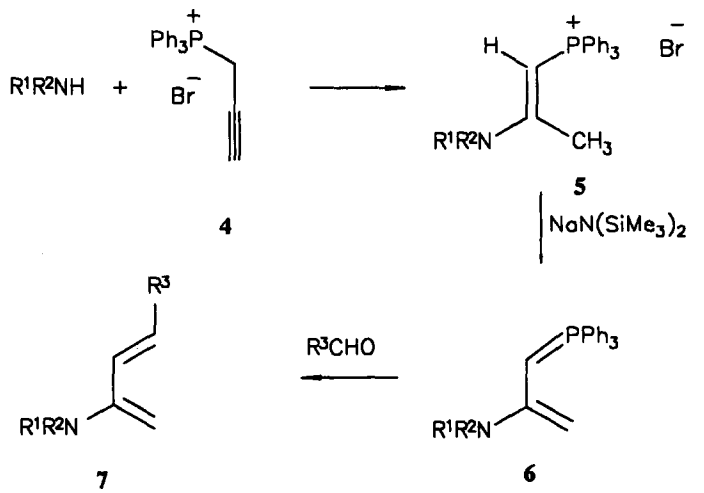
 # Dedicated to Professor Dr. Rolf Huisgen on the occasion of his 70th birthday

On the other hand, we have used phosphorylted enamines as starting materials in the preparation of acyclic and cyclic derivatives [7]. Continuing our interest in the reactivity of phosphorus substituted enamines and in the synthesis of 2-amino-1,3-butadienes, we describe here a very easy preparation of them from comercially available starting reagents, as propargyltriphenylphosphonium bromide, amines and aldehydes, through Wittig reaction of the phosphoranes **6** generated *"in situ"* from the β-enamino phosphonium salts **5** with aldehydes.

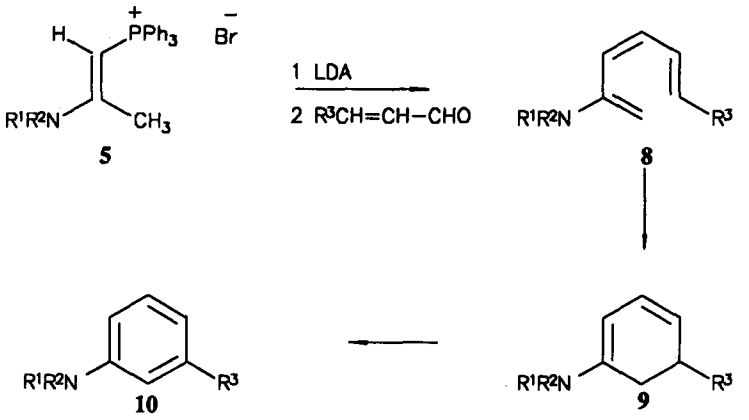


The preparation of the desired β-enamino phosphonium salts **5** was very easily accomplished in very high yields through nucleophilic addition of secondary amines to propargyltriphenylphosphonium bromide **4** [7] in refluxing of acetonitrile. Spectral data are in agreement with structure **5** [9]. Thus, the meyhyl group of **5a** appears at δ = 1.91 and 21.6 ppm in the ^{1}H- and ^{13}C-NMR spectra, respectively; while the enaminic CH give a ^{1}H-resonance at δ = 3.96 ppm ($^2J_{PH}$ = 14.0 Hz) and a ^{13}C-resonance at δ = 58.5 ppm ($^1J_{PC}$ = 121.7 Hz.) as well resolved doublets.

Wittig reaction of phosphoranes **6** generated *"in situ"* from β-enamino phosphonium salts with a base such as sodium hexamethyldisilazide [10] followed by addition of aliphatic, carbocyclic, heteroaromatic and aromatic aldehydes (see Table) and after heating the reaction mixture 12 h at 60°C leads to 2-amino-1,3-butadienes **7** [11] in excellent yields. Spectroscopic data are consistent with the proposal structure, in which vicinal coupling constants of 15.7 Hz for the vinylic protons of **7a** evidenced *E* configuration of the carbon-carbon-double bond.



However, α,β-unsaturated aldehydes show different reactivity. Thus, treatment of β-enamines **5** with lithium diisopropylamide (LDA) in THF followed by addition of crotonaldehyde or cinnamaldehyde and heating the reaction mixture at 60°C did not give the acyclic conjugated enamines **8**, but the substituted cyclic amines **9** were obtained instead. Amines **9** were easily oxidised to aromatic amines **10** in the presencae of air. Formation of amines **9** could be explained through Wittig reaction of the phosphoranes **6** with the aldehydes followed by an electrocyclic ring closure.



The synthesis described in this comunication provides an easy and efficient entry to 1-amino-1,3-butadienes, making use of readily available starting materials. These systems could be key intermediates in the synthesis of natural products [2].

Table of compounds **5, 7 and 10** prepared

	R^1		R^2	R^3	yield (%) [a]	m.p (°C) [b]
5a		$(CH_2)_5$			93	231-232(d)
5b	Et		Et		92	178-179(d)
7a		$(CH_2)_5$		Pr^i	81	oil
7b		$(CH_2)_5$		Cyclohex.	82	oil
7c		$(CH_2)_5$		Et	54	oil
7d		$(CH_2)_5$		3-thienyl	80	oil
7e		$(CH_2)_5$		3-pyridyl	81	oil
7f		$(CH_2)_5$		Ph	88	oil
10a		$(CH_2)_5$		Me	84	oil
10b	Et		Et	Ph	85	oil

[a] All the new compounds was characterized by high resolution NMR analysis

[b] Oils isolated after "trap to trap" high vacuum destillated (10^{-5} torr).

Acknowledgement. Financial support of this work by Comisión Asesora de Investigación Científica y Técnica (CAICYT) is grateful acknowleged.

REFERENCES AND NOTES

1.- For a review see: R.R Schmidt, *Acc. Chem. Res.*, **1986**, *19*, 250.

2.- S.J. Danishefsky, M.P. DeNinno, *Angew. Chem*, **1987**, *99*, 15. C.M. Andersson, A.Hallberg, *J. Org. Chem.*, **1989**, *54*, 685.

3.- W.H. Pearson, K.C.Lin, Y.F. Poon, *J. Org. Chem.*, **1989**, *54*, 5814.
A. Padwa, W.H. Bullock, A.D. Syszlewski, *J. Org. Chem.*, **1990**, *55*, 955.

4.- J.E.Bäckvall, N.A. Plobeck, S.K. Juntunen, *Tetrahedron Lett.*, **1989**, *30*, 2589
A.Padwa, B. Harrison, S.S. Murphree, P.E. Yeske, *J. Org. Chem.*, **1989**,*54*, 4232.

5.- J. Barluenga, F. Aznar, M.P. Cabal, F.H. Cano, M.C. Foces. *J. Chem. Soc., Perkin Trans 1*, **1990**. 633
J. Barluenga, F. Aznar, M.P. Cabal, C. Valdés, *Tetrahedron Lett.*, **1989**, *31*, 5923

6.- J. Barluenga, F. Aznar, R. Liz, M.P. Cabal, *J. Chem.Soc. Chem. Commun.*, **1985**, 1375

7.- J. Barluenga, F. López, F. Palacios, *Tetrahedron Lett.*, **1988**, *29*, 4863. J. Barluenga, F. López, F. Palacios, F. H. Cano, M. C. Foces-Foces, *J. Chem. Soc. Perkin Trans I*, **1988**, 2329.

8.- H. Hoffmann., H. Förster, *Tetrahedron Lett.*, **1964**, *17*, 983.

9.- Spectral data for **5a**: δ_H (300 MHz, $CDCl_3$): 1.72(m, 6H, $3CH_2$), 1.91(s, 3H, CH_3), 3.58 (m, 4H, $2CH_2$), 3.96 (d, 1H, $^2J_{PH}$= 14.0 Hz, CH=), 7.5-7.8(m, ArH); δ_C (75 MHz, $CDCl_3$): 21.6 (d,CH_3, $^3J_{PC}$=6.4Hz.), 22.7(CH_2), 24.7(CH_2), 47.7(CH_2), 58.5(d, CH=, $^1J_{PC}$= 121.7 Hz.), 121.9-133.3 (CArom), 162.8(d, =CN, $^2J_{PC}$=13.9 Hz.); δ_P (120 MHz, $CDCl_3$): 17.7 ppm

10.- When other bases such as *BuLi, Bu'Li* and *LDA* were used lower yields of 2-aminodienes **7** were obtained.

11.- Spectral data for **7a**: δ_H (300 MHz, $CDCl_3$): 1.02(d, 6H, $^3J_{HH}$ = 6.7 Hz, 2 CH_3),1.45-1.65 (m, 6H, $3CH_2$), 2.33(m, 1H, CH), 2.83(m, 4H, $2CH_2$), 3.95(s, 1H, CH=), 4.17(s, 1H, CH=), 5.80 (d, 1H, $^3J_{HH}$=15.7 Hz.), 5.92(dd, 1H,$^3J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 5.9 Hz, CH=); δ_C (75 MHz, $CDCl_3$): 22.2(CH_3), 24.4(CH_2), 25.8(CH_2), 30.9(CH), 50.7(CH_2), 89.5(CH_2=), 126.1(CH=), 139.1(CH=), 155,7(NC=).

(Received in UK 19 September 1990)